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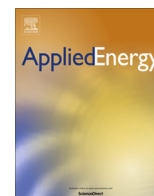http://eprints.nottingham.ac.uk/40075/1/Wenbin-AppliedEnergyPaper-OpenAccess-2016.pdf

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Parametric study on the regeneration heat requirement of an amine-based solid adsorbent process for post-combustion carbon capture

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HIGHLIGHTS

- Revised equation of regeneration heat is proposed to include process related factors.
- Key parameters (e.g. heat of adsorption) experimentally determined.
- Parametric analysis made on both physical properties and process related parameters.
- Calculated regeneration heat for PEI/silica sorbent based system is 2.46 GJ/tCO$_2$.
- Working capacity, moisture adsorption and heat recovery are most influential factors.

ABSTRACT

The thermal energy required for regeneration of CO$_2$-rich adsorbents or absorbents is usually regarded as the most important criterion to evaluate different materials and processes for application in commercial-scale CO$_2$ capture systems. It is expected that the regeneration heat can be greatly reduced by replacing the mature aqueous monoethanolamine (MEA) technology with amine-based solid adsorbents capturing systems, due to the much lower heat capacity of solid adsorbents comparing to aqueous MEA and the avoidance of evaporating a large amount of water in the regenerator. Comparing to the MEA technology, the regeneration heat for solid adsorbent based systems has not received adequate attention especially on the impacts of process related parameters. Further, the methodologies used in previous investigations to calculate the regeneration heat may have deficiencies in defining the working capacities, adopting proper heat recovery strategies and/or evaluating the effect of moisture co-adsorption. In this study, an energy equation to calculate the regeneration heat has been revised and proposed to systematically evaluate the most important parameters affecting the regeneration heat, including the physical properties of the adsorbents and process related variables including the heat of adsorption, specific heat capacity, working capacity, moisture adsorption of the polyethyleneimine (PEI)/silica adsorbent, the swing temperature difference and the degree of heat recovery. Based on the parametric analysis, the calculated regeneration heat for the PEI/silica adsorbent based system is found to be around 2.46 GJ/tCO$_2$, which is much lower than the value of 3.9 GJ/tCO$_2$ for a typical aqueous MEA system and is also lower than 3.3 GJ/tCO$_2$ for an advanced MEA system. Sensitivity analysis of all the parameters has also been conducted and the results have shown that working capacity, moisture adsorption and heat recovery ratios are the most influential factors. With more proficiency and development in the energy efficient process designs, the advantages of a solid adsorbent based capturing system over typical MEA systems will be justified.

1. Introduction

Carbon Capture and Storage (CCS) from large point sources such as coal-fired power plants has been considered as one main technology to address rising CO$_2$ emissions as a result of continual fossil fuel utilization. Post-combustion capture (PCC) is a front runner for future commercial deployment of CCS in fossil fuel power

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plants, partly due to the fact that it can be retrofitted to the existing power plants. However, implementing CCS in fossil fuel power plants will result in an increase in the cost of electricity by up to 80% according to the current state-of-art technology [1–3] as the energy requirement for the whole CCS chain is high. For capture, the energy consumption is the sum of the thermal energy needed to regenerate the solvents/sorbents and the electrical energy required to operate pumps, blowers and fans. Further, energy is also required to compress the CO_2 to the final pressure required for transport and storage. Among these energy requirements for capture, the regeneration heat greatly impacts on the operational costs and the overall energy efficiency of the CCS-integrated power plant. In principle, the regeneration heat for a post-combustion CO_2 capture process with an aqueous solvent or a solid adsorbent includes the sensible heat required to elevate the solvent or sorbent to the desorption temperature, the latent heat required to overcome the endothermic reaction responsible for removing CO_2 from the solvent or sorbent and the latent heat for water vaporization.

Monoethanolamine (MEA) scrubbing technology has been successfully demonstrated in gas- and coal-fired plants with power outputs as large as 30–40 MW [4] and is treated as a benchmark technology for CO_2 capture from large-scale power plants [3,5–7]. A regeneration heat of 4.2 GJ/tCO$_2$ was proposed by Chapel et al. [8] for their optimized MEA-based CCS process – Econamine FG™ technology. Alie et al. [9] concluded that the lowest energy requirement of 4 GJ/tCO$_2$ could be achieved at lean solvent loading between 0.25 and 0.30 mol CO_2/mol MEA using a flow sheet decomposition method. Singh et al. [10] modelled the MEA process for a 400 MWe coal fired power plant and estimated the specific thermal energy requirement to be 3.8 GJ/tCO$_2$. In average, a value of 3.9 GJ/tCO$_2$ can be regarded as the energy requirement for a benchmark MEA based capture system.

The high energy requirement makes CCS process costly. Technology developers and researchers have concentrated their effort on developing new and/or optimizing existing technologies to minimize the regeneration heat. For example, Li et al. [11] investigated the electrical efficiency of the supplementary fired combined cycles integrated with the MEA-based capture system and concluded that the modifications can reduce the efficiency penalty caused by CO_2 capture to only 2.6% of Lower Heating Value (LHV). The Fluor Econamine FG Plus™ technology requires a much lower energy requirement of 3.24 GJ/tCO$_2$ [12] which is achieved by optimizing process configurations such as split flow, absorber intercooling and improved solvent formulation. Similarly, Abu-Zahra et al. [6] also proposed a 30% MEA absorption system with the thermal energy requirement of 3.3 GJ/tCO$_2$ achievable through optimizing the lean solvent loading, the amine solvent concentration as well as the stripper operating pressure. Therefore, a representative value of 3.3 GJ/tCO$_2$ has been adopted in this paper as the energy requirement for an advanced MEA based system with optimized process configurations. Although it has been reported that some other amine aqueous solutions based systems may lead to an even lower energy requirement, such as 2.5–2.6 GJ/tCO$_2$ [13], the 30% MEA absorption system is the most well-known and mature technology and therefore is used as a reference for comparison with our proposed polyethyleneimine (PEI)/silica adsorbent based system.

In recent years, a great deal of effort has been made on the development of solid sorbents for PCC due to their potential advantages in lower regeneration heat requirement, the avoidance of amine evaporation and reduced corrosion. Among these solid sorbents, various amine-based solid adsorbents have been shown to be promising CO_2 capture materials due to their high adsorption capacities and reliable regeneration for coal and natural gas fired power plants and even for air capture [14–21]. Apart from a few

pilot trial tests recently conducted [22,23], most experimental investigations on amine-based solid adsorbents have been limited to relatively small scales such as thermal gravimetric analyzer (TGA) and recently in fluidized bed reactors [21,24,25]. The status of the research on PCC with solid adsorbents is still at the early stages of R&D and therefore there is significant deficiency in the data availability especially in the context of a specific process. Theoretical estimation of energy penalties for the PCC process is essential before scaling up to a sub-commercial demonstration or a full-scale commercial trial.

By replacing the amine carrier from aqueous water to solid substrates, it is believed that the regeneration heat can be greatly reduced due to the much lower heat capacity of solid sorbents comparing to aqueous MEA and the avoidance of evaporating significant amounts of water in the regenerator. However, unlike MEA technology, which has been extensively investigated for process optimization to minimize the regeneration heat, a comprehensive knowledge on the regeneration heat of solid adsorbent system is lacking, especially concerning the impact of key parameters. Gray et al. [17] proposed a simplified energy equation to calculate the regeneration heat for a solid adsorbent based system:

$$Q_r = \Delta H_a + mC_{p,s}\Delta T \tag{1}$$

where Q_r (kJ/mol) is the regeneration heat, ΔH_a (kJ/mol) is the heat of adsorption, m (kg) is the solid mass, $C_{p,s}$ (kJ/kg K) is the solid specific heat capacity and ΔT (K) is the change in temperature. Using a similar equation, Sjostrom and Krutka [26] estimated the regeneration heat for different types of amine based adsorbents and found the values varying in a large range of 1.9–6.1 GJ/tCO$_2$ depending on the amine types, regeneration conditions and working capacities. Based on Eq. (1), Heesink et al. [27] estimated a regeneration heat of 1.7 GJ/tCO$_2$ for their amine based solid adsorbents assuming a very high working capacity of 3.1 mmol/g. By adding a term of vaporization heat of water into Eq. (1), Quang et al. [28] estimated the regeneration heat to be in the range of 2.1–4.2 GJ/tCO$_2$ for their PEI impregnated adsorbent, also with an assumption of high working capacity of 3–3.4 mmol/g. Applying Eq. (1), Li et al. [29] calculated the regeneration heat for PEI/silica adsorbents with different molecular weights of PEI and found the values to be around 1.7–1.8 GJ/tCO$_2$.

The heat of adsorption of an amine-based solid adsorbent depends upon the amine type, molecular weight and adsorption conditions. However, this parameter has not received adequate attention by experimental studies as it is often theoretically estimated by different models [19,30,31,32]. Working capacities may have been over-estimated by some calculations without considering the regeneration conditions [29,33]. Process related parameters, such as the heat recovery of the sensible heat, are not included in Eq. (1) while a sensible heat recovery ratio of 90% is assumed in most MEA technologies. Hedin et al. [34] have reviewed the adsorbents for post-combustion capture using rapid Temperature Swing Adsorption (TSA) and emphasized that the heat integration of the adsorption-driven processes with the power plant is crucial in ensuring the economy of the CO_2 capture technology. Besides, the effect of moisture co-adsorption on the regeneration heat has not been considered by many previous investigations [17,26,33] except the recent study by Quang et al. [28] who found that the regeneration heat increased significantly from 2.1 GJ/tCO$_2$ to 4.2 GJ/tCO$_2$ when the moisture uptake increased from 3 to 10 wt%.

The value of regeneration heat is a primary parameter for process designs including regenerator and steam extraction system. An accurate calculation of regeneration heat is essential to justify the advantages of a solid adsorbent system over the traditional MEA technology in terms of energy efficiency. It needs a comprehensive understanding of not only the physical properties of the

solid adsorbent but also the process-related parameters linked to a specific process design. The methodologies adopted by the previous investigations to calculate the regeneration heat have certain deficiencies in determination of the material characteristics and process-related parameters. A theoretical guidance is crucial to compare the impacts of all the parameters on the regeneration heat and to direct how to reduce the energy penalty more efficiently. In this study, a thermal energy balanced equation has been first proposed to clarify and re-evaluate the regeneration heat by using clearly defined working capacity, inclusion of moisture co-adsorption and the degree of heat recovery. TGA and Differential Scanning Calorimetry (DSC), as well as theoretical modelling, have been applied to determine the characteristics of the material. Several process-related parameters have also been verified in a purpose-built laboratory scale fluidized bed reactor using kg scale adsorbent. To the best of our knowledge, a sensitivity analysis of various parameters on the regeneration heat has been carried out for the first time to further elaborate the uncertainties arising from the current limited knowledge. This study demonstrates that not only working capacity, but also the moisture adsorption and the degree of heat recovery are the most influential factors affecting the regeneration heat for the PEI/silica adsorbent based system investigated.

2. Thermal energy requirement for regeneration

The regeneration heat has a crucial impact on the CO_2 capture cost and therefore is regarded as the most important criterion to evaluate the economic performance of a commercial scale CO_2 capture plant. In principle, it comprises the sensible heat which is necessary to bring the adsorbent from the adsorption temperature to the regeneration temperature in TSA technologies; the latent heat of desorption of which absolute value equals to the heat of adsorption and which is needed to overcome the chemical bonding strength between the adsorbed CO_2 and the adsorbent; and thirdly the latent heat which is induced by vaporization of water in the solvent or moisture in the adsorbent. The calculation of regeneration heat for a solid adsorbent based system using TSA technology can accordingly be revised from Eq. (1) and expressed as:

$$Q_r = \frac{1-\alpha}{q_w} C_{p,s}(T_{de} - T_{ad}) + (1-\beta)\Delta H_a + (1-\gamma)\frac{Q_v f_{H2O}}{q_w} \qquad (2)$$

where Q_r (kJ/mol) is the regeneration heat requirement; q_w (mmol/g) is the working capacity of the adsorbent under given working conditions; α, β, γ are the fractions of heat recovery from sensible heat, heat of adsorption and vaporization heat respectively which can be realized through proper process designs; $C_{p,s}$ (kJ/kg K) is the specific heat capacity of the adsorbent; T_{ad} and T_{de} (K) are the temperatures of adsorption and desorption processes respectively; ΔH_a (kJ/mol) is the absolute value of heat of adsorption; Q_v (kJ/kg) is the vaporization heat of water which equals to 2257.6 kJ/kg at atmospheric pressure; and f_{H2O} is the moisture uptake in the adsorber (i.e. H_2O adsorbed simultaneously with the CO_2 adsorption which will be evaporated in the regenerator at regeneration temperatures higher than 373 K at atmospheric pressure). Among the parameters in Eq. (1), some are physical properties of the adsorbents such as $C_{p,s}$ and ΔH_a, some are operational parameters related to the specific designed process such as α, β and $T_{de} - T_{ad}$ while others are determined by both the adsorbent characteristics and process design such as q_w and f_{H2O}.

The authors have developed a PEI/silica based adsorbent and used this adsorbent for the following experimental research and parametric analysis. All variables involved in Eq. (2) have been theoretically or experimentally investigated in this study so that the advantage of this adsorbent based capture system in terms of regeneration heat requirement can be quantified and compared with those of MEA based systems.

3. Experimental section

3.1. Materials

The adsorbent used in this study was synthesised by impregnating different mass ratios of 40%, 50%, 60% PEI (supplied by Sigma–Aldrich, UK) into an inorganic mesoporous silica support which has a BET surface area of approximately 250 m^2/g, pore volumes of 1.7 cc/g and a mean pore diameter of approximately 20 nm [15]. PEIs of two molecular weights (MW), 1800 and 600, have been used for the preparation of the adsorbent. A 20 kg quantity of the PEI/silica adsorbent with a 40% mass ratio of PEI to silica and having a MW of 1800 of PEI was produced in collaboration with an industrial partner for the fluidized bed tests while small quantities containing different PEI mass ratios with varying MWs were prepared by the authors in the laboratory for TGA and DSC measurements. Details of characterization of the PEI/silica adsorbent by TGA, NMR, DRIFT, XPS and a fluidized bed reactor can be found in previous publications [14,15,20,21].

3.2. TGA testing

To measure the CO_2 uptake, a TGA (TA Q500 model) was used to assess the adsorption capacity with small amounts of sample (20–30 mg).

3.2.1. Isothermal tests

In a typical isothermal TGA test, the sample was heated up to 383 K in N_2 to desorb any pre-adsorbed CO_2 and moisture. The sample was then cooled down to the desired adsorption temperature when a mixture of CO_2 and N_2 was fed to the TGA furnace. The uptake of CO_2 by the adsorbent sample was determined by the mass increase during the adsorption stage. Five different gas mixtures containing 5%, 15%, 30%, 50% and 100% CO_2 balanced with N_2 were used for the isothermal tests. The adsorption of N_2 on the PEI/silica adsorbent can normally be neglected under the experimental conditions used. The adsorption temperature was selected as 343 K since the specific PEI/silica adsorbent performs best at this temperature as determined previously [21].

3.2.2. Isobaric tests

In order to reveal the dependence of CO_2 uptake on the adsorption temperature for a given CO_2 partial pressure, TGA measurements using slow heating rate (0.1 K/min) under isobaric conditions have been carried out to derive the pseudo-equilibrium capacities. These tests were run from ambient temperature to 423 K. One CO_2/N_2 gas mixture (15% CO_2) and pure CO_2 were used for two sets of isobaric tests to simulate the gas compositions for adsorption and desorption processes, respectively.

3.2.3. Cyclic adsorption tests

To investigate the cyclic performance and the thermal stability of the PEI/silica adsorbent, a series of 50 continuous cycles has been carried out in the TGA. Each cycle includes an adsorption process at 343 K with 15% CO_2 balanced by N_2, and a desorption process with pure N_2 as the sweep gas. The temperature of the TGA furnace was swung between the adsorption and desorption temperatures for each cycle. Two temperatures, 393 and 403 K, were used for desorption to ascertain the temperature effect on the thermal degradation. No moisture was present during both adsorption and desorption in these cyclic tests.

3.2.4. Moisture adsorption tests

The moisture content of actual flue gas in coal-fired power plant is typically 8–10 vol%. When the dry adsorbent is returned to the adsorber after regeneration, moisture adsorption may occur at the same time as CO_2 adsorption. In order to assess the moisture adsorption capacity and its effect on the CO_2 adsorption, the TGA has been modified to be able to introduce a controlled level of moisture into the furnace. The carrier gas was first diverted into a saturator which was immerged in a temperature controlled water bath. Then the carrier gas was redirected back into the TGA furnace through a heated line without condensation. The adsorption temperature for both moisture and CO_2 adsorption in the TGA furnace is 343 K. After PEI/silica adsorbent was dried at 383 K for half an hour, humidified N_2 containing around 9 vol% of moisture (RH = 30%) was fed into the TGA furnace until the sample was saturated with moisture. Subsequently, a mixture of 15% CO_2 and the same amount of moisture balanced by N_2 was fed into the TGA for co-adsorption of moisture and CO_2 until they were both saturated. Three continuous cycles have been conducted to check the repeatability.

3.3. DSC measurements

The DSC measurements have been carried out using an advanced SENSYS evo TG-DSC instrument which was manufacturer calibrated before the use. This instrument provides accurate sensors around the reactor furnace, together with a symmetrical microbalance to give combined TG and DSC signals for simultaneous measurements of the mass change and heat flow during adsorption. The heat of adsorption can then be derived in terms of the heat released per mole of CO_2 adsorbed. The experimental procedure is basically similar to that used in the isothermal TGA tests. The effects of PEI loading, molecular weight, adsorption temperature and CO_2 partial pressure on the heat of adsorption have been evaluated by using various samples under different adsorption conditions.

Before specific heat capacities of the PEI/silica adsorbents were determined, a blank test was first conducted with the empty crucible. Samples were dried at 383 K with N_2 for half an hour prior to the continuous C_p measurements where the furnace temperature is slowly increased from 303 to 403 K at a heating rate of 1 K/min.

3.4. Fluidized bed testing

A Bubbling Fluidized Bed (BFB) reactor was designed and manufactured for the purpose of investigating CO_2 capture from simulated flue gas mixtures using solid adsorbents. An electrically heated moisture saturator with separate temperature controls is used to generate the desired level of moisture for the adsorption and desorption. Up to 2 kg of PEI/silica adsorbent was loaded into the BFB reactor for continuous 60 cycles of adsorption and desorption tests. The adsorption was conducted at 343 K with 15% CO_2 balanced by N_2 while the desorption was conducted at 403 K with pure N_2 as the sweep gas. Dry simulated flue gas as well as humidified flue gas containing around 8.8 vol% moisture were used to evaluate the moisture effect on the cyclic performance of the PEI/silica adsorbent. More details of the fluidized bed tests can be found in Zhang et al. [21].

4. Parametric analysis of factors affecting regeneration heat

4.1. Heat of adsorption ΔH_a

The magnitude of the heat of adsorption can be estimated from either various equilibrium models or by direct calorimetry measurement. An atomistic modelling of CO_2 chemisorption in aqueous solutions of primary and tertiary amines using DFT (Density Functional Theory)-based quantum chemical solvation has revealed that the heat of absorption is around 80 kJ/mol during carbamate formation and around 65 kJ/mol during bicarbonate formation [35]. By using a 2-L reaction calorimeter, Kim and Svendsen [36] measured the heat of absorption of CO_2 with aqueous MEA to be around 80–85 kJ/mol at 313 K, 90–95 kJ/mol at 353 K and 100–110 kJ/mol at 393 K.

There have also been some measurements or estimation of the heats of adsorption for various amine-based solid sorbents in the literature as summarized in Table 1.

According to the references cited in Table 1, the heats of adsorption of amine-based solid adsorbents vary over a wide range from around 40 to 90 kJ/mol, depending on the amine type, substrate type and immobilization methodology.

4.1.1. Langmuir isothermal equations fit

At equilibrium, the chemical adsorption of CO_2 on a solid adsorbent can be modelled using Langmuir isothermal adsorption equation [41]:

$$\theta = \frac{q}{q_{sat}} = \frac{b(T)p}{1 + b(T)p} \qquad (3)$$

where θ is the fraction of the surface covered by CO_2 molecules, q (mmol/g) is the adsorption capacity while q_{sat} (mmol/g) represents the saturated amount of adsorption when the solid surface is fully covered by one layer of CO_2 molecules. p (bar) is the partial pressure of CO_2. b (bar^{-1}), the affinity coefficient between CO_2 and the adsorbent, is dependent on temperature T (K) as follows:

$$b(T) = b_0 \exp\left(\frac{\Delta H_a}{RT}\right) \qquad (4)$$

where b_0 (bar^{-1}) is the pre-exponential constant for the affinity coefficient, ΔH_a (kJ/mol) is the absolute value of heat of adsorption and R is the universal gas constant (8.3145 J/mol K).

Eq. (3) can be re-written as follows so that the parameters of q_{sat} and b can be obtained by regression from experimental data:

$$\frac{p}{q} = \frac{1}{b(T)q_{sat}} + \frac{1}{q_{sat}}p \qquad (5)$$

Table 1
Heat of adsorption for various amine-based solid sorbents.

| Ref.	Types of solid adsorbents	ΔH_a (kJ/mol)	Methodology
Knowles et al. [30]	Functionalized mesoporous silica with 3-aminopropyltriethoxysilane	60	Calculated
Gray et al. [17]	Immobilized PEI on polystyrene (PS), silicon dioxide (SiO_2) and polymethyl-methacrylate (PMMA) based substrates	43–63	Measured
Belmabkhout and Sayari [31]	Mesoporous silica based TRI-PE-MCM-41	90	Calculated
Sun et al. [37,38]	Impregnation of as-purchased MEA onto TiO_2	81	Model fitted
Ebner et al. [19]	PEI immobilized into a CARiACT G10 silica substrate	50	Model fitted
McDonald et al. [39]	Alkylamine-appended metal–organic framework	61	Calculated
Li et al. [29]	Branched and linear PEIs on silica base	64–71	Measured
Mebane et al. [40]	Mesoporous silica supported amine	61	Calculated
Spenik et al. [25]	Immobilized amine on a mesoporous silica	66	Data fitted
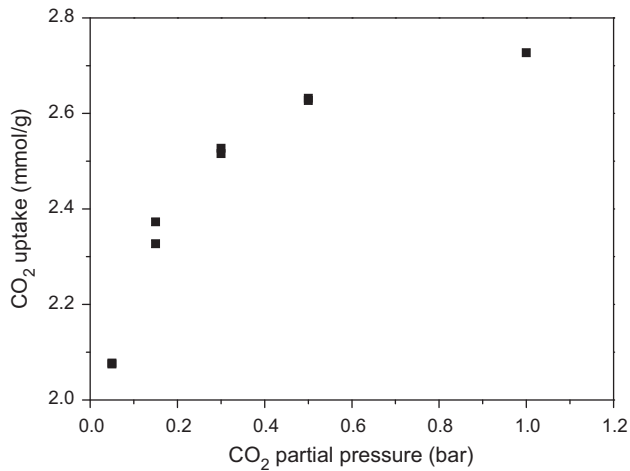
Fig. 1. TGA results of CO_2 uptake using various CO_2 partial pressures for PEI/silica adsorbent (isothermal at 343 K).

Fig. 3. Isobaric CO_2 uptake with temperature for the PEI/silica adsorbent (0.15 bar CO_2 partial pressure, 0.1 K/min of heating rate).

Fig. 1 illustrates isothermal CO_2 uptakes at 343 K at CO_2 partial pressures of 0.05, 0.15, 0.3, 0.5, 1 bar for the PEI/silica adsorbent determined by TGA. Fig. 2 shows the linear fit of these TGA data to the Langmuir isothermal Eq. (5). This linear fit implies that the Langmuir equation can provide a good representation of the CO_2 adsorption thermodynamics for the PEI/silica adsorbent, in agreement with Fauth et al. [42]. The two parameters in Eq. (5) can then be determined by the linear function shown in Fig. 2.

$$q_{sat} = 2.78 \text{ mmol/g}, \; b(343) = 40.23 \text{ bar}^{-1}$$

Fig. 3 illustrates a typical plot of isobaric CO_2 uptake for the PEI/silica adsorbent under 0.15 bar CO_2 partial pressure. The CO_2 uptake reaches its peak value at around 340 K and drops to its minimum value at around 397 K. The observed CO_2 uptake at temperatures above 397 K is attributed to the formation of secondary urea groups, as suggested by Drage et al. [15], leading to the irreversible loss of CO_2 capacity. The existence of such a maximum adsorption uptake has also been verified by a number of researchers for various amine based adsorbents [16,43,44]. However, based on Eqs. (3) and (4), an increase of temperature will lead to a lower adsorption capacity. This is true when the adsorption behavior is only controlled by thermodynamics as the adsorption of CO_2 on solid surface is obviously an exothermal reaction. Diffusion control may
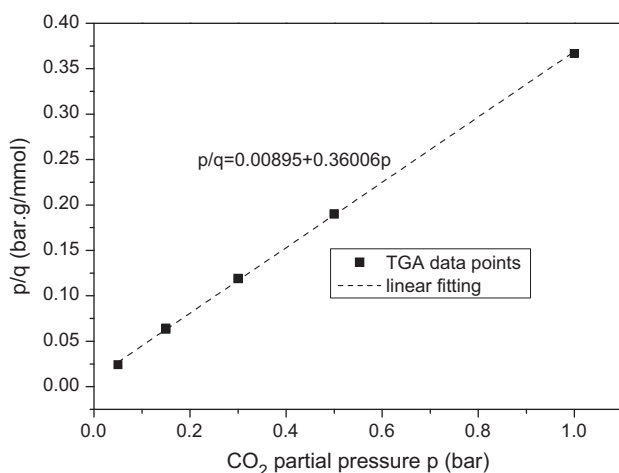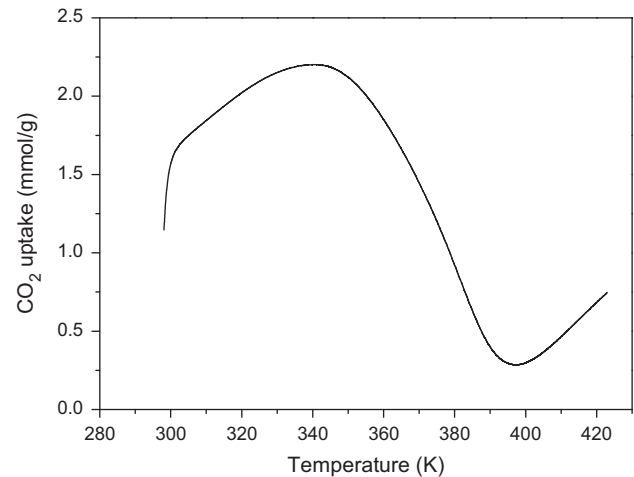
be dominant, especially at temperatures below 343 K. The maximum adsorption capacity is most likely to be a compromise between diffusion and thermodynamically controlled mechanisms.

Eq. (4) can be further re-written as:

$$\ln(b) = \ln(b_0) + \frac{\Delta H_a}{R} \cdot \frac{1}{T} \tag{6}$$

As shown in Fig. 4, the slow heating results by TGA (Fig. 3) can be fitted by a linear function. The temperature range of 353–393 K, which is believed to be under thermodynamic control as explained earlier, is selected for the data fitting. Based on the interception and slope of the linear function, it can be derived that:

$$b_0 = 1.976 \times 10^{-12} \text{ bar}^{-1}, \; \Delta H_a = 88.4 \text{ kJ/mol}$$

4.1.2. DSC measurements

In order to obtain more accurate data on the heat of adsorption and also to verify the validity of Langmuir isothermal models, the heats of adsorption for the PEI/silica adsorbent have been measured by the instrument SENSYS evo TG-DSC.

PEI/silica adsorbents of three PEI loadings (40%, 50% and 60%) and two MWs (1800 and 600) have been tested at three adsorption temperatures (298, 323 and 343 K) and two CO_2 concentrations
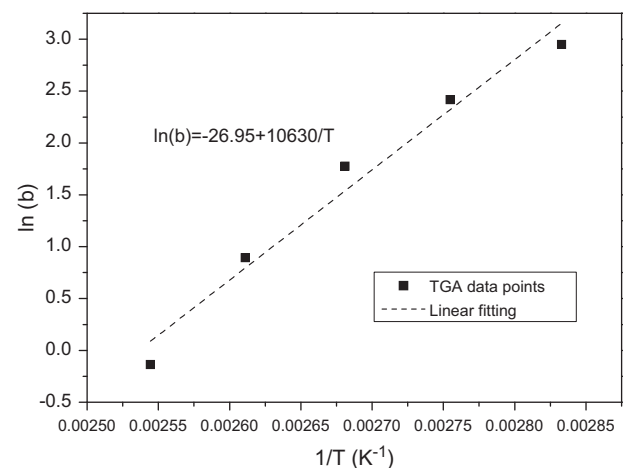

Fig. 2. Linear fitting of TGA data to Langmuir isothermal equation.

Fig. 4. Linear fitting of b_0 and ΔH_a using TGA results for the PEI/silica adsorbent (CO_2 partial pressure: 0.15 bar).

(5% and 15%). The samples used in the DSC measurements are denoted as PEI'W'-MW'X'-R'Y'-'Z'K, where W denotes the PEI loading, X denotes the molecular weight, Y denotes the CO_2 concentration and Z denotes the adsorption temperature. Three repeat tests were conducted on the sample PEI40-MW1800-R15-343K and the results were 93.7, 95.0, and 95.5 kJ/mol, indicating that the measurement errors were within the range of ±1.5%.

As indicated in Fig. 5, it is clear that the heats of adsorption are higher at elevated temperatures, which is in agreement with the temperature dependence identified for MEA by Kim and Svendsen [36]. Adsorbents with higher PEI loadings seem to have higher heats of adsorption, especially at the lowest adsorption temperature of 298 K. PEI/silica samples with the same MW of 1800 but different PEI loadings and different adsorption temperatures show higher values of heat of adsorption in 15% CO_2, compared to the lower concentration of 5% (Fig. 6). By comparing a pair of samples PEI40-MW600-343K and PEI40-MW1800-343K, or the pair of PEI40-MW600-323K and PEI40-MW1800-323K under 15% CO_2, it is apparent that the lower MW PEI has the higher heat of adsorption which might be due to the higher content of primary amine groups in the lower MW sample (600). This is in agreement with the findings on the heat of adsorption for PEI/silica adsorbents with different MW reported by Li et al. [29]. For all samples, the measured heats of adsorption by TG-DSC in this study fall within the range of 85–103 kJ/mol, which is comparable to the value for 30% aqueous MEA (92 kJ/mol at 353 K) measured by Kim and Svendsen [36] but is higher than most of the reported results shown in Table 1. High heat of adsorption provides the potential for high CO_2 adsorption capacity over a wide range of operating conditions and system designs such as for capturing CO_2 directly from ambient air [20] but it also brings the associated disadvantage of high energy requirements for releasing the CO_2 during regeneration.

4.2. Specific heat capacity $C_{p,s}$

Heat capacity of a specific sorbent/solvent is an essential parameter for the process design in calculating the heat duty in the regenerator and the heat flux in the heat exchangers for recovering the sensible heat contained in the hot sorbent/solvent. In a typical aqueous MEA based absorption system, the sensible heat can account for up to 40% of the total regeneration heat [45], mainly due to the large amount of water present. By replacing aqueous amines with solid sorbents, the heat capacity can be greatly reduced. Yang and Hoffman [46] adopted the value of
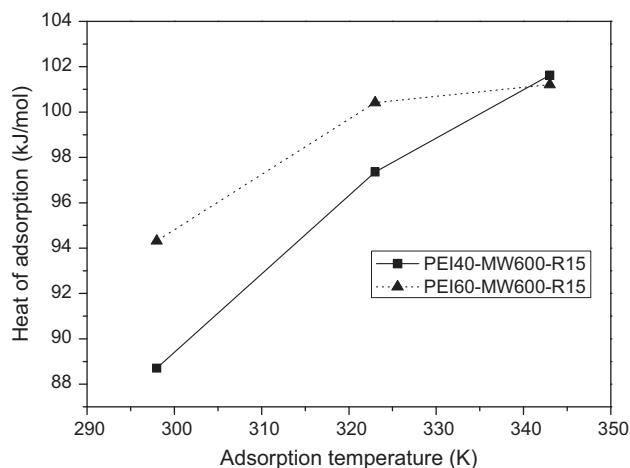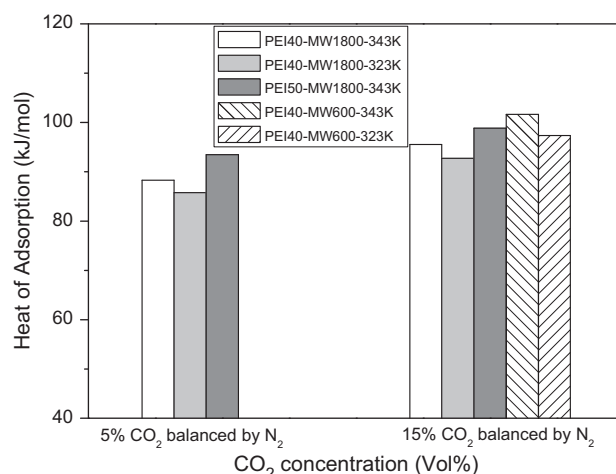

Fig. 6. Effect of CO_2 concentration on heat of adsorption for PEI/silica samples with different molecular weights and adsorption temperatures.

1.926 J/g K for the specific heat capacity of solid sorbents used in their exploratory design study on reactor configurations. Pirngruber et al. [32] estimated a value of 1.25 J/g K for the PEI based solid sorbents in a theoretical analysis of the energy consumption of post-combustion CO_2 capture processes. More recently, Quang et al. [28,47] used a micro-reaction calorimeter to measure the heat capacities of precipitated silica-based solid sorbents impregnated with various types of amines over the temperature range of 303 to 363 K, with moisture content varying from 0% to 15%.

The temperature-dependant specific heat capacities of the PEI/silica adsorbent have been determined by TG-DSC and the results are illustrated in Fig. 7 and compared with the reference data from Quang et al. [28]. The heat capacities of sample PEI40-MW1800 tend to increase as temperature increases from 303 to 383 K, which is in accordance with previous studies on the heat capacities of amine systems [28,48,49]. The values are considerably lower than that for 30 wt% MEA solvent which is around 4.0 J/g K. The PEI-PS-60 in Ref. [28] which has a higher PEI loading of 60% has a higher value of heat capacity, owing to the higher heat capacity of PEI comparing to silica. The C_p data between the adsorption and desorption temperature (which are about 343 K and 403 K respectively) are more important as the sensible heat are calculated in this temperature window. According to the DSC results, the average specific heat capacity for sample PEI40-MW1800 within the temperature range of 343–403 K is around 1.81 J/g K.
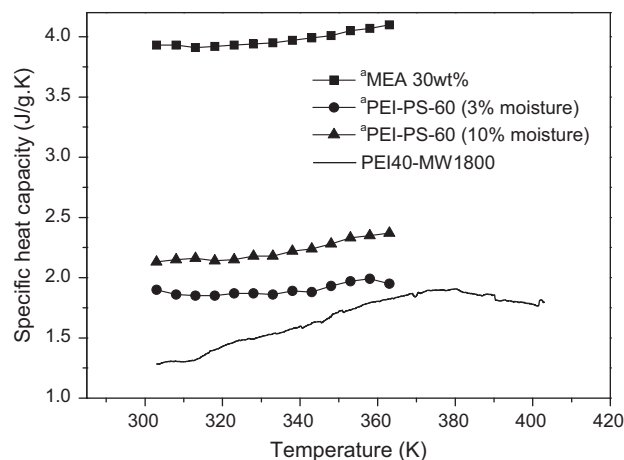

Fig. 5. Effect of temperature on heat of adsorption for samples with different PEI loadings.

Fig. 7. DSC measurements of specific heat capacity of PEI40-MW1800 and comparison with reference data ([a] data from [28]).

4.3. Temperature swing difference $T_{de} - T_{ad}$

The dependence of adsorption capacities on temperature, as revealed in Fig. 3, makes it possible to regenerate PEI/silica adsorbents by TSA where the adsorption temperature is T_{ad} and the desorption temperature is T_{de}. A number of researchers have proposed an optimum adsorption temperature T_{ad} of around 343 K for PEI impregnated solid adsorbents [16,21,43,44]. As the magnitude of sensible heat is proportional to the temperature difference, from this viewpoint, selection of as low as possible T_{de} is beneficial in requiring less regeneration heat, assuming that this selection will not cause a significant decrease in working capacity q_w. More importantly, PEI impregnated adsorbents suffer from serious thermal degradation when they are exposed to high desorption temperature for long periods of operation, probably due to the formation of urea groups especially in the absence of moisture. Fig. 8 shows the TGA results of continuous 50 dry cycles for the PEI/silica adsorbent using two desorption temperatures of 393 and 403 K. After 50 cycles, the PEI/silica adsorbent has suffered a relative loss of 15% from their initial adsorption capacity using 403 K as the desorption temperature, comparing with a lower loss of 7.7% under 393 K.

On the other hand, the endothermic nature of desorption implies that a higher temperature is favorable to obtain more complete desorption at a higher rate. This is beneficial to achieve a high working capacity. In addition, solids residence time in the regenerator can be largely reduced with higher desorption rates, which in turn can reduce the inventory solid mass, the reactor dimension and the corresponding capital and operational costs. The thermal degradation of PEI/silica adsorbents at 403 K can be effectively alleviated by introducing a certain amount of moisture during adsorption and desorption. Fig. 9 shows the adapted results from previous work on a fluidized bed reactor for evaluating the cyclic performance of the PEI/silica adsorbent [21]. The normalized CO_2 adsorption capacity is defined as a dimensionless factor by dividing the capacity of any cycle to the initial capacity of the first cycle. Introduction of around 8.8 vol% of moisture, which is a similar level of moisture present in the real flue gas from coal-fired power plants, has been proved to be able to stabilize the adsorption capacity after a total number of 60 cycles.

Therefore, the desorption temperature needs to be carefully selected by considering a number of factors including sensible
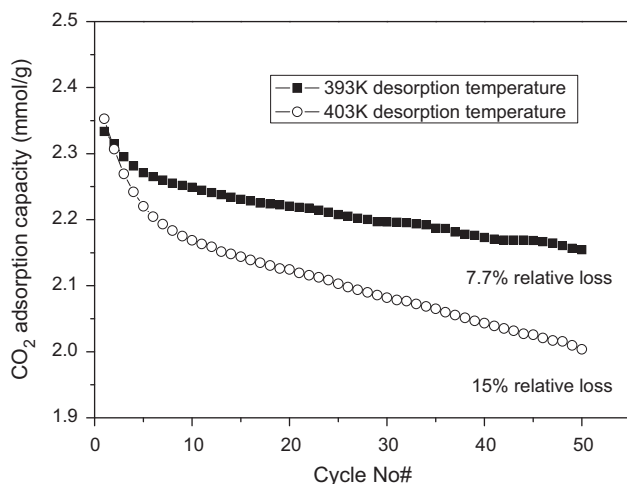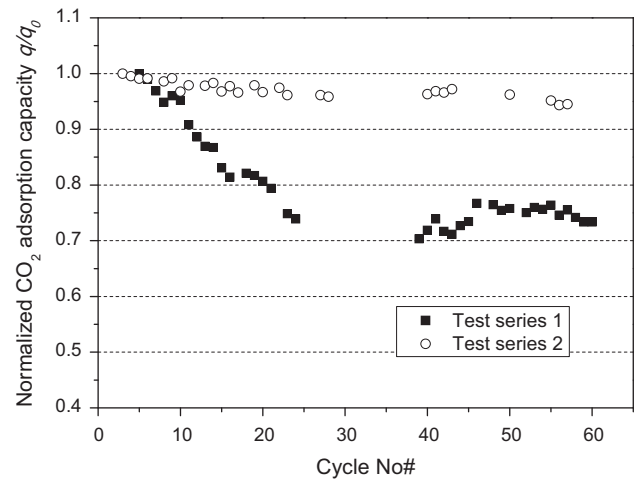

Fig. 9. Cyclic normalized CO_2 adsorption capacities of PEI/silica adsorbent obtained from the fluidized bed tests (adsorption at 343 K with 15% CO_2 balanced with N_2, desorption at 403 K with pure N_2 as sweep gas. Test series 1: first 24 cycles without moisture while all the following cycles with 8.8 vol% moisture; Test series 2: 8.8 vol% moisture was present from the first cycle. Data adapted from previous publication [21]).

heat, thermal degradation, working capacity, desorption rate and moisture effect. In this study, T_{ad} is selected as 343 K and T_{de} is selected as 403 K, giving a temperature swing difference of 60 K.

4.4. Working capacity q_w

The equilibrium CO_2 adsorption capacity, determined by TGA under isothermal conditions, is usually regarded as an indicator to evaluate the performance of a specific solid sorbent. For a practical application, the solid sorbents are being circulated continuously between the adsorber and the desorber. The term of "working capacity q_w" can be defined as the difference between the CO_2 loading at the end of the adsorption stage and the CO_2 loading at the end of desorption stage, i.e.

$$q_w = q_{ad} - q_{de} = q_{sat}\left(\frac{b(T_{ad})p_{ad}}{1 + b(T_{ad})p_{ad}} - \frac{b(T_{de})p_{de}}{1 + b(T_{de})p_{de}}\right) \qquad (7)$$

where p_{ad} and p_{de} are the CO_2 partial pressure for adsorption and desorption, respectively.

Although nitrogen was used as the sweep gas during desorption in our previous studies using TGA and the fluidized bed [20,21], it is impractical to use the same regeneration strategy as the product gas needs to have a high purity of CO_2 for further compression and storage. Using pure CO_2 as the sweep gas during desorption can yield high purity CO_2. However, this may result in serious thermal degradation and lower working capacities [15,24,50]. Pure steam has also been proposed as the sweep gas [17,51] to alleviate thermal degradation at the cost of a higher thermal energy penalty and additional devices for water condensation from the desorbed CO_2 stream. In addition, long periods of exposure to steam may decrease the CO_2 uptake of PEI/silica adsorbents as observed in recent studies [50,52,53]. Therefore, regeneration strategies using steam as the sweep gas still need further investigation. In the following analysis, pure CO_2 is proposed as the sweep gas.

Fig. 10 shows a series of Langmuir isothermal curves at different temperatures. The parameters in the Langmuir model are adopted from the calculations in Section 4.1.1 (ΔH_a = 88.4 kJ/mol, q_{max} = 2.78 mmol/g, b_0 = 1.976 × 10^{-12} bar^{-1}). This figure can be used to predict the working capacity under certain working conditions. For example, if the adsorption is conducted at 343 K with 15% CO_2 present in the flue gas (corresponds to point A in

Fig. 8. Cyclic CO_2 adsorption capacities of the PEI/silica adsorbent under 393/403 K desorption temperature by TGA (adsorption at 343 K with 15% CO_2 balanced with N_2, desorption conducted with pure N_2 as sweep gas, no moisture present during adsorption and desorption).
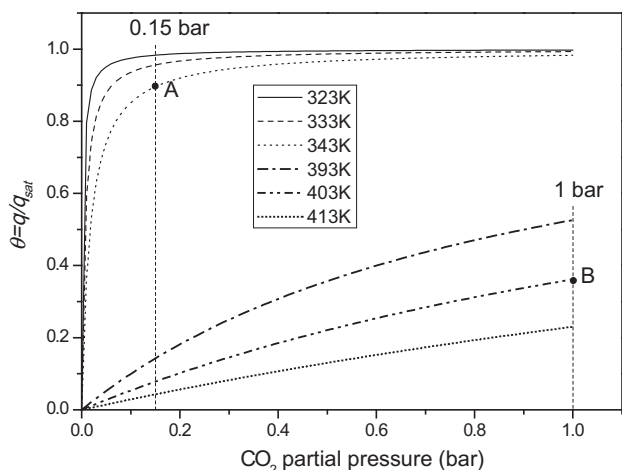
Fig. 10. Langmuir model predictions of working capacity for PEI/silica adsorbents (ΔH_a = 88.4 kJ/mol, q_{max} = 2.78 mmol/g, b_0 = 1.976 × 10^{-12} bar^{-1}, values adopted from Section 4.1.1).

Fig. 10) and the desorption is conducted at 403 K with pure CO_2 as the sweep gas (corresponds to point B in Fig. 10), the difference between points A and B is: $\Delta\theta$ = 0.534, which gives a working capacity of q_w = 1.48 mmol/g.

The working capacity of the PEI/silica adsorbent can also be estimated from the pseudo-equilibrium capacities obtained from TGA isobaric tests. Fig. 11 shows one case where adsorption is conducted at the optimum temperature of 340 K with 15% CO_2 (corresponds to point A) while desorption is conducted at 403 K with lowest CO_2 uptake using pure CO_2 as the sweep gas (corresponds to point B). The difference in CO_2 uptake between points A and B can be considered as the working capacity and is estimated as 1.35 mmol/g.

The estimated working capacity in this case is around 60% of the maximum CO_2 uptake at 340 K under 15% CO_2. A higher working capacity means that less amount of adsorbent is required for CO_2 adsorption for a given amount of CO_2 to be captured, leading to less sensible heat requirement and also less electrical energy to physically circulate the adsorbent between adsorption and desorption reactors. Therefore, the optimal working conditions of adsorption and regeneration strategies need to be further investigated to obtain as high working capacity as possible.
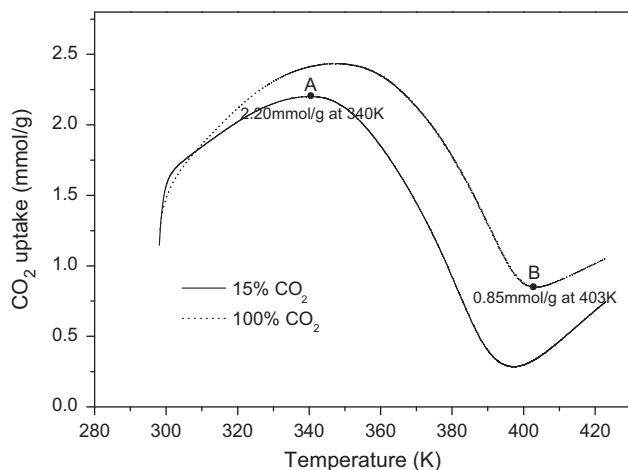
4.5. Moisture adsorption f_{H2O}

Amine based solid sorbents normally contains a number of hydrophilic silanol and amino groups which have a strong affinity to water. They can adsorb moisture from humid surroundings at room temperature and therefore usually contain a certain amount of moisture. Further, moisture adsorption can occur in the adsorber when the adsorbent is in contact with the real flue gas containing a certain level of moisture (typically 8–10 vol% for coal-fired power plants if the moisture has not been removed prior to entering the adsorber). The moisture adsorbed during the time spent in the adsorber increases the apparent heat capacity of the sorbents and more importantly results in additional requirement of vaporization heat during regeneration. There are only a few studies, such as Quang et al. [28], which have addressed the effect of moisture adsorption on the regeneration heat.

For the specific PEI/silica adsorbent investigated here, co-adsorption of moisture and CO_2 on the dry sample in TGA has been carried out and the results are shown in Fig. 12. The adsorption of moisture onto the adsorbent surface reached its equilibrium value of around 2 wt% after about 10 min for the PEI/silica adsorbent under the specific adsorption conditions. One can expect that this value will be lower when CO_2 is present due to competitive adsorption, or if the solids residence time in the adsorber can be less than 10 min. It can also be seen that the subsequent CO_2 adsorption capacity has not been much affected by the pre-adsorption of moisture (around 10 wt%, i.e. 2.27 mmol/g, comparing to TGA result of 2.20 mmol/g in Fig. 11). The negligible effect of moisture co-adsorption on CO_2 uptake has also been verified by other researchers [50,54] and this may imply that there is little competition for adsorption sites between CO_2 and H_2O. Changes in adsorption conditions (such as moisture content in flue gas and the adsorption temperature) may significantly change the moisture adsorption capacity, especially when the relative humidity approaches 100% in the moisture saturated flue gas [54].

4.6. Heat recovery fractions α, β, and γ

The aqueous amine scrubbing technology has been commercialized and significant improvements have been made in terms of heat recovery, turbine and flow-sheet modifications. By improving the internal heat recovery in the steam and solvent circulation cycles for a coal-fired power plant, the efficiency penalty for amine scrubbing can be effectively reduced [55]. Optimized process configurations have also been proposed by Amrollahi et al. [56] for

Fig. 11. Estimation of working capacity using pseudo-equilibrium capacities obtained from the isobaric TGA tests (adsorption at 340 K with 15% CO_2 and desorption at 403 K with pure CO_2 as the sweep gas).
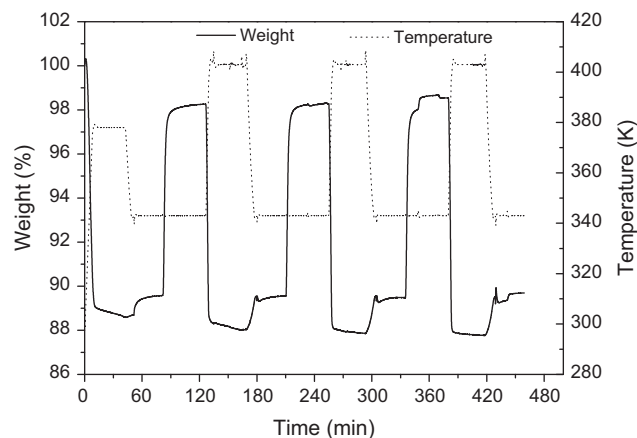

Fig. 12. Co-adsorption of moisture and CO_2 on dry PEI/silica adsorbent for continuous 3 cycles at 343 K in humidified carrier gas containing 9 vol% moisture.

natural-gas-fired power plant, which include improved technologies such as absorber inter-cooling and lean vapor recompression.

Comparing to the large number of studies on low temperature solid sorbent materials development aiming at achieving high adsorption capacities, process and system design and modelling as well as optimization have received little attention. Park et al. [57] recently proposed a multi-stage process configuration for large scale power plant carbon capture with solid adsorbents. Heat integration is realized by direct heat exchange between the hot and cold solid adsorbents and also by indirect heat exchange using heat transfer media. Additional heat recovery is realized from the exhaust gas streams coming from the cyclones. Following Park's work, Kim et al. [58–60] developed a process model to assess the economic feasibility of various process designs including moving bed, bubbling bed and fast fluidized bed applying amine based solid sorbents. A parameter, "degree of heat integration (DHI)", was defined to evaluate the performance and energy efficiency of the whole system:

$$DHI\ (\%) = \frac{\text{Recovered thermal energy by heat integration}}{\text{Total regeneration energy w/o any heat recovery}} \times 100 \tag{8}$$

They concluded that the DHI value for the optimized multi-stage system can be enhanced up to 80%.

Thermal energy recovery from sensible heat, latent heat in both adsorbent and moisture is the most effective way to reduce the total regeneration energy requirement. The recovery ratio α of sensible heat is assumed to be 75% for the PEI/silica based capture system, the same as that suggested by Veneman et al. [33], which is lower than the value of 90% used for the lean/rich solvent heat exchanger in a typical aqueous MEA scrubbing process [56]. Due to the difficulty in recovering the heat of adsorption from the flue gas exiting the adsorber at low temperatures of around 343 K, recovery ratio β is assumed to be 0.25 for the nominal case. The recovery ratio γ of the vaporization heat is assumed to be 0.5 which can be technically realized by condensing the evaporated steam at the exit of the desorber.

5. Discussions on regeneration heat requirement

Nominal values of parameters in the calculation of regeneration heat for the PEI/silica adsorbent capture system are summarized in Table 2 based on the above parametric analysis. Values of heat of adsorption ΔH_a and heat capacity $C_{p,s}$ are adopted for the sample of PEI40-MW1800-R15-343K.

By substituting the nominal parameters into Eq. (2), the components of sensible heat, heat of adsorption, vaporization heat and the total regeneration heat are calculated for the PEI/silica CO_2 capture system and compared with the benchmark aqueous MEA 30% system. Results are included in Table 3 and illustrated in Fig. 13. It can be seen that the PEI/silica based system has a big advantage in

Table 2
Nominal parameters adopted for calculating regeneration heat for the PEI/silica based capturing system.

ΔH_a (kJ/mol)	95
$C_{p,s}$ (kJ/kg K)	1.81
ΔT (K)	60
q_w (mmol/g)	1.35
f_{H2O}	0.02
α	0.75
β	0.25
γ	0.5

Table 3
Calculation of regeneration heat (GJ/tCO2) for the PEI/silica based system compared with the benchmark aqueous MEA 30% system [28].

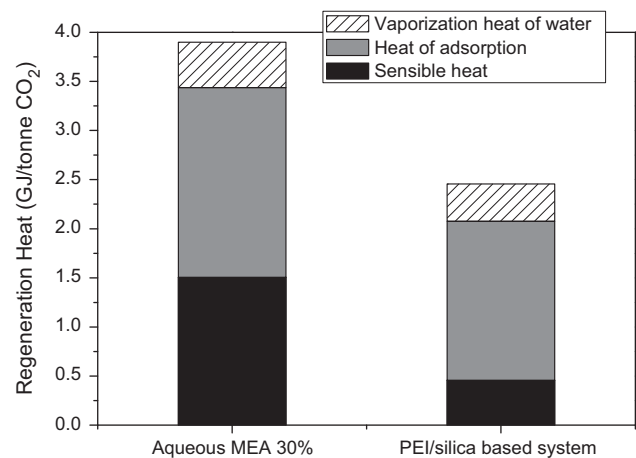| Types of heat	Benchmark 30% MEA system	PEI/silica CO_2 capture system
Sensible heat	1.505	0.457
Heat of adsorption	1.932	1.619
Vaporization heat	0.462	0.380
Total regeneration heat	3.90	2.46

Fig. 13. Comparison of regeneration heat requirement for the PEI/silica CO_2 capture system with the benchmark 30% MEA system.

saving sensible heat, given the fact that the specific heat capacity of the solid sorbent is much lower than aqueous MEA. The other two components for the PEI/silica system, the heat of adsorption and vaporization heat, are slightly lower than the MEA system for the given recovery ratios listed in Table 2. In total, the regeneration heat for the proposed PEI/silica CO_2 capture system is 2.46 GJ/tCO2, which represents a relative reduction of 37% from the value of 3.90 GJ/tCO2 for the benchmark MEA system [28]. It is also 25% lower than the value of 3.30 GJ/tCO2 which is adopted in this paper for the advanced and state-of-art MEA scrubbing technology, as proposed by Abu-Zahra et al. [6] and IEA [12].

Sensitivity analyses of the influence of all parameters on the value of regeneration heat have been conducted within varying ranges of the nominal values listed in Table 2 and the results are summarized in Fig. 14. It is assumed that all parameters are independent of each other although it may not be exactly true. For example, changes in heat of adsorption and the temperature swing difference may cause changes in working capacity. However, this effect has been ignored for simplicity with the sensitivity analysis.

Fig. 14(a) shows the effect of heat of adsorption on the regeneration heat. As the measurement results of heat of adsorption for the PEI/silica adsorbent by TG-DSC in this study are larger than most reported values, only negative variations up to −50% of the nominal value have been considered, which gives a much lower regeneration heat of 1.65 GJ/tCO2. The regeneration heat is less sensitive to the specific heat capacity and swing temperature difference, as shown in Fig. 14(b) and (c). Relative variations in both $C_{p,s}$ and ΔT between ±50% have resulted in a relative variation of only ±9% in the regeneration heat. Within the variation ranges investigated, all values of regeneration heat for the solid sorbent capture system are lower than the advanced MEA system.

Increasing working capacity is regarded as one of the most effective ways to reduce the regeneration heat. As shown in
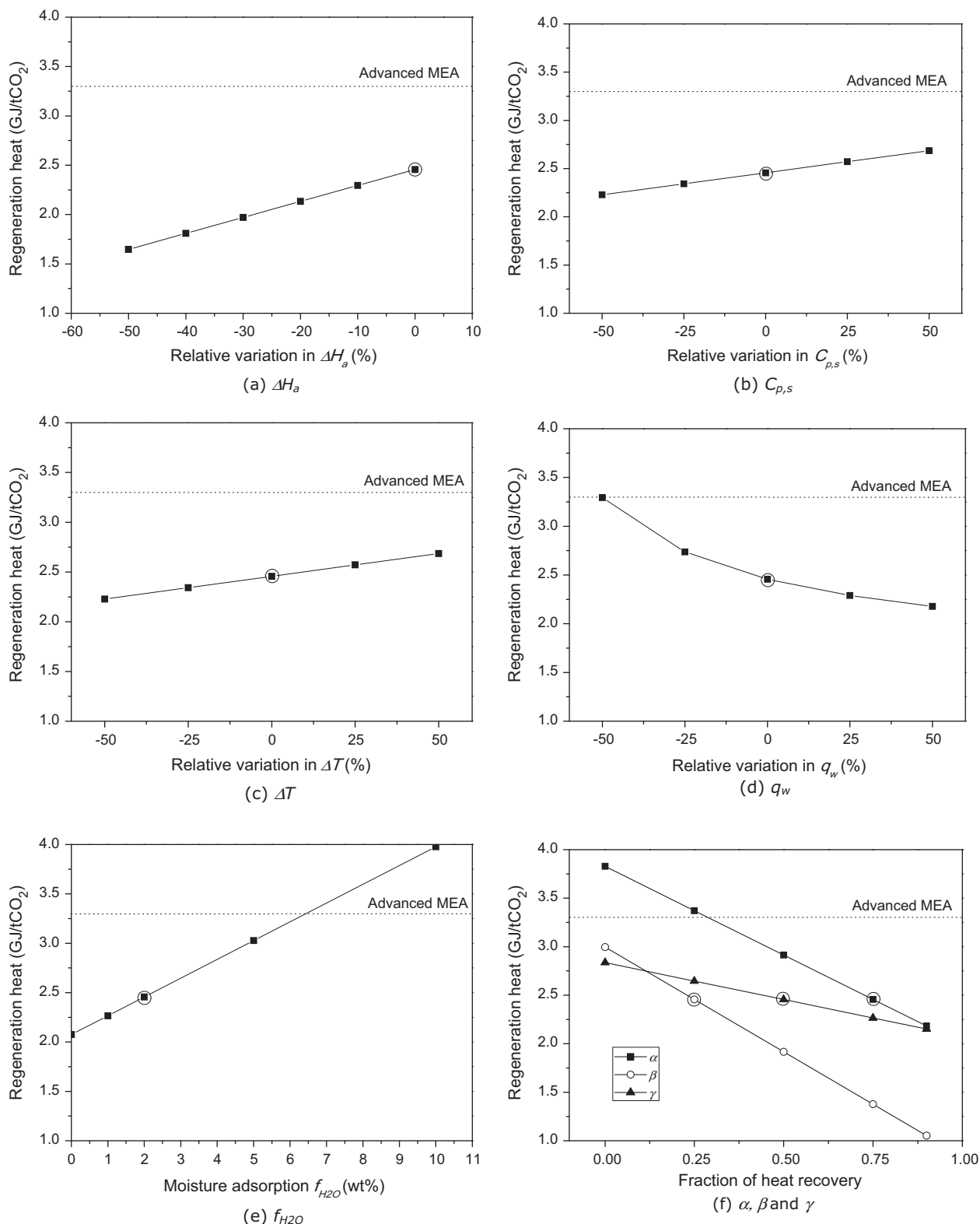
Fig. 14. Sensitivity analysis of parameters affecting the regeneration heat (data point within a circle denotes the value which corresponds to the nominal condition specified in Table 2).

Fig. 14(d), 50% improvement on the working capacity (from 1.35 to 2.025 mmol/g) only gives a relative reduction of 11% in the regeneration heat (from 2.46 to 2.18 GJ/tCO$_2$). When the working capacity is as low as 0.675 mmol/g, which is a 50% relative reduction, the calculated regeneration heat is much higher and it is comparable to the advanced MEA system.

The amount of moisture adsorbed has a significant effect on the regeneration heat if all of the adsorbed moisture is assumed to be vaporized as steam in the desorber. For an absolute reduction of the moisture adsorption from 2 wt% to zero as shown in Fig. 14 (e), the regeneration heat is reduced to 2.08 GJ/tCO$_2$, which represents 15.5% reduction. This implies that eliminating moisture

adsorption is more effective than improving the working capacity by 50% for reducing the regeneration heat. If moisture adsorption reaches 10 wt%, the calculated regeneration heat would have exceeded the regeneration heat requirement of the baseline MEA system. Therefore, it is vital to effectively control the moisture adsorption in the adsorber, for example, by necessary surface modifications, or by controlling the solid residence time in the adsorber. Additional heat recovery facilities on the CO_2 stream leaving the desorber is also essential to recover the condensation heat of the evaporated steam.

The degree of heat recovery from all heat components in Eq. (2) depends on proper process design. As shown in Fig. 14(f), the regeneration heat is reduced to 2.18 GJ/tCO_2 if 0.9 of the recovery ratio α can be realized as for the typical MEA system. The PEI/silica sorbent capture system will not show any advantages over advanced MEA systems if the sensible heat recovery ratio α is lower than 0.25. As the heat of adsorption contributes more than 60% of total regeneration heat, the value of regeneration heat can be vastly reduced down to 1.92 GJ/tCO_2 if the recovery ratio β can be improved up to 0.50. The improvement on increasing the heat recovery ratio γ is less significant as vaporization heat contributes least in the total regeneration heat. By assuming the nominal values of α = 0.75, β = 0.25 and γ = 0.5, the calculated DHI from Eq. (8) is 61%, which is still much lower than the value of 80% concluded by Kim et al. [59,60] for their process design. This implies that by using energy efficient process designs such as the multi-stage fluidized bed process concept proposed by Kim et al. [59,60], the regeneration heat of 2.46 GJ/tCO_2 with the assumptions made in this study can be realized.

6. Conclusions and further discussion

Parametric analysis of various factors influencing the regeneration heat required for CO_2 capture using the PEI/silica adsorbent has been made in this study. A revised equation for calculating regeneration heat has been proposed to evaluate the effects of physical properties of the adsorbent as well as process related parameters. The proposed equation is based on a fundamental thermal energy balance and, therefore, it is applicable not only to the specific PEI/silica adsorbent in this study but also to all solid adsorbents based CO_2 capture systems using TSA technology. It provides a theoretical guidance for comparing the advantages of various solid adsorbents and different processes in terms of thermal efficiencies. As the regeneration heat represents the most important energy penalty for a practical power plant integrated with CCS facilities, the equation can be further used to evaluate the net plant efficiency penalties.

This paper has provided a case study based on the specific PEI/silica adsorbent and several assumed parameters. The calculated regeneration heat is 2.46 GJ/tCO_2 which is lower than 3.9 GJ/tCO_2 for a typical aqueous MEA system and is also lower than 3.3 GJ/tCO_2 for advanced MEA systems. To ensure the reliability of the results, most parameters in the equation have been verified by different means including TGA, DSC, measurements in a laboratory fluidized bed and theoretical modelling as well. The calculated regeneration heat is however higher than some reported values for amine based solid adsorbents [27,29]. This is mainly due to the fact that our measured heat of adsorption is higher than most reported values. The DSC measurements have revealed that the heat of adsorption is dependent on the amine loadings, molecular weight, adsorption temperature and CO_2 partial pressure. It can be expected that it is also dependent on the amine types as well. For a practical CO_2 capture application where CO_2 partial pressure can differ significantly, the heat of adsorption for the selected adsor-

bent should be carefully tailored to make a compromise between the energy penalties and capture efficiency and kinetics.

There are several uncertainties in the current parametric analysis as revealed by the sensitivity analysis. The first comes from the difficulty in estimating the working capacities accurately. Unlike the equilibrium CO_2 adsorption capacities which are achieved under ideal working conditions and long reaction time, the working capacities need to be determined in the context of a specific process where working conditions of both adsorption and desorption, solid residence times in both adsorber and desorber, regeneration strategies and cyclic performance all have crucial influences. Although this study has provided two means of estimation of the working capacities, more experimental work under simulated practical working conditions should be the future research emphasis. It should also be noted that the relationship between the regeneration heat and the working capacity is not linear. Further improvement on the working capacity (50% increase) can only give rise to a relatively small decrease in the regeneration heat (11%).

The second uncertainty comes from the moisture adsorption on the solid adsorbents. Although it is measured in this study that the moisture adsorption capacity for the PEI/silica adsorbent under the specified conditions is only 2 wt%, this may significantly increase if the relative humidity is higher or if the amine types have stronger water affinity. The solid adsorbent based CO_2 capture system will be economically unfeasible if the moisture adsorption capacity is as high as 10 wt%. For such a practical system, additional facilities or surface modification techniques should be in place to control the moisture adsorption.

The third uncertainty comes from the estimation of the heat recovery ratios although this study has assumed conservative values for these parameters. Improvement on the heat recovery can significantly reduce the regeneration heat. However, there have been very few studies on the designing and configuring of a practical or pilot scale process which can realize high integration of heat recovery except for the very recent publications such as Park et al. [57], Kim et al. [59,60], Veneman et al. [61], Schony et al. [62] and Proll et al. [63], although most of these are limited to theoretical or feasibility study.

Apart from materials development, investigations into the process related parameters should receive much more attention for practical carbon capture applications using solid adsorbents. These should include more experimental work on evaluating the working capacities in a specific process, restraining moisture co-adsorption in the adsorber and designing of the high degree heat integral processes and facilities. These priorities are believed to be of importance for the future demonstration and commercialization of CCS technology.

Acknowledgements

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